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Ion-Solvent Interaction in Mixed Solvents: Viscosity of Lithium, Sodium & Potassium Bromides in N,N-Dimethylformamide-Water Mixtures

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The viscosities of LiBr, NaBr and KBr in N,N-dimethylformamide-water mixtures have been measured at 25° and the results have been analysed by Jones-Dole equation $\eta/\eta^\circ = 1 + Ac^{1/2} + Bc$. The coefficients A and B are obtained graphically from the plot of $[(\eta/\eta^\circ - 1)/c^{1/2}]$ against c, as well as from the least squares method. The values of B coefficient indicate ion-solvent interaction. B-coefficient for LiBr and NaBr in water-DMF increases with increasing concentration of DMF whereas in the case of KBr it diminishes first and then increases.

THE viscosity measurements of lithium bromide, sodium bromide and potassium bromide in dimethylformamide-water mixtures have been carried out at 25°C. The data have been interpreted in terms of Jones-Dole[1] equation

$$\eta/\eta^\circ = 1 + Ac^{1/2} + Bc \qquad ...(1)$$

where η and η° are the viscosities of the solution and solvent respectively; c is the molar concentration of electrolyte; and A and B are constants. The coefficient A is due to the contribution from interionic electrostatic forces[2-4] and B gives the measure of the order or disorder introduced by the ions into the solvent structure.

A review of the literature shows that no general theory has yet been developed for B-coefficient, however, it is a manifestation of ion-solvent interaction[5]. In the present investigation interest, therefore, centres on the coefficient B. The nature of B-coefficient as pointed out by Cox and Wolfenden[6] is attributed to its specific additive character depending on the constituent ions. On the other hand, Asmus[7] used the entropy of hydration to correlate ionic B values and recently a single linear relationship between ionic B values and molar entropy of hydration has been obtained by Nightingale[8].

Materials and Methods

Lithium bromide (E. Merck), sodium and potassium bromides (BDH, Analar) were recrystallized from triply distilled conductivity water [$(0{\cdot}7 \pm 0{\cdot}1) \times 10^{-6}$ mhos], dried and kept in a vacuum desiccator. N,N-Dimethylformamide (BDH) was purified by the method of Sears and coworkers[9]. The water-DMF solvent mixtures containing 15·0, 30·0, 45·0, 60·0, 70·0, 85·0 and 100·0% by weight of dimethylformamide were prepared at least four hours in advance to avoid air bubbles which are released after mixing process. The temperature in the Gallenkamp water-bath was maintained at 25° ± 0·01°. Cannon-Ubbelhode viscometer[10] (No. 50, A703) was used for viscosity measurements. The viscometer with the viscosity constant of (0·003910 centistokes/sec) was used for viscosity measurement. The time of flow of the liquid was measured with a stop watch accurate to 0·1 sec. The viscometer was well cleaned, dried and standardized with conductivity water before use. At least six determinations were made for each solution and difference of any two readings did not exceed 0·2 sec. This leads to an error of ±0·04 to ±0·08%. Therefore, the overall uncertainty in the viscosity was estimated to be less than 0·1%. The densities of solutions were measured with the aid of a pyknometer of 20 ml capacity in the constant temperature bath. The stem of the pyknometer was graduated in 0·01 ml so that the volume could be read up to 0·005 ml. Densities obtained are precise to ±0·0002 g/ml. The viscosities of the solutions were calculated with reference to carbon dioxide free pure water at 25° which is 0·8903 cp (ref. 11). Measuring vessels and reagent bottles used were all of pyrex and Jena glass.

Results and Discussion

Viscosities of the mixed solvents as well as of those containing salts under study were measured and results have been analysed by Jones-Dole equation (1). In actual calculations, Eq. (1) is transformed to

$$(\eta/\eta^\circ - 1)/c^{1/2} = A + Bc^{1/2} \qquad ...(2)$$

The plot of $(\eta/\eta^\circ - 1)/c^{1/2}$ versus $c^{1/2}$ was linear, the intercept and the slope of which gave the values of A and B respectively. The values of these constants have been calculated by the least squares method also and are reported in Table 1 alongwith the graphical values. The theoretical value of A is computed using Falkenhagen and Vernon[4] expression for uni-univalent electrolyte. The calculated values of A and the literature values of B are in fair agreement with our experimental results (Table 1).

TABLE 1 — VALUES OF COEFFICIENTS *A* AND *B* FOR LiBr, NaBr and KBr IN WATER-DMF MIXTURES AT 25°

Constant		% DMF in water-DMF mixtures							
		0·0	15	30	45	60	70	85	100
		LITHIUM BROMIDE							
A	Graphical value	0·0068 (0·0072)*	0·0075	0·0048	0·0125	0·0210	0·0050	0·0065	0·0140
	Least squares value	0·0062	0·0076	0·0054	0·0124	0·0193	0·0016	0·0042	0·0141
B	Graphical value	0·0926 (0·106)*	0·1065	0·1469	0·1825	0·2600	0·4000	0·5795	0·7962
	Least squares value	0·0926	0·1051	0·1471	0·1809	0·2667	0·4166	0·5856	0·7918
		SODIUM BROMIDE							
A	Graphical value	0·0068 (0·0062)*	0·0110	0·0040	0·0178	0·0220	0·0025	0·0068	0·0480
	Least squares value	0·0071	0·0115	0·0040	0·0186	0·0231	0·0009	0·0050	0·0469
B	Graphical value	0·0468 (0·044)*	0·0566	0·1030	0·1161	0·1500	0·2588	0·3680	0·6428
	Least squares value	0·0470	0·0535	0·1029	0·1140	0·1433	0·2667	0·3756	0·6807
		POTASSIUM BROMIDE							
A	Graphical value	0·0045 (0·0049)*	0·0260	0·0160	0·0260	0·0198	0·0020	0·0025	—
	Least squares value	0·0047	0·0271	0·0166	0·0260	0·0185	0·0002	0·0049	—
B	Graphical value	−0·0565 (−0·048)*	−0·0763	−0·0325	−0·0276	0·0381	0·1437	0·2944	—
	Least squares value	−0·0540	−0·0828	−0·0303	−0·0290	0·0420	0·1518	0·2843	—

*Values in parentheses are literature values at 25° (ref. 11 and 13).

The viscosity of dimethylformamide-water mixtures increases gradually with increasing percentage of the former and approaches maximum and thereafter decreases (Fig. 1). The viscosity maximum has been obtained for aq. DMF containing 60·0% of DMF, in agreement with the findings of earlier investigators[12].

It is observed that *B*-coefficient for LiBr and NaBr increase with increasing percentage of DMF in water-DMF mixtures whereas for KBr it first diminishes and then increases (Table 1, Fig. 1).

According to Stokes and Mills[11] the viscosity of a dilute electrolytic solution incorporates that of solvent plus the contribution from four other sources. Thus,

$$\eta = \eta^{\circ}+\eta^{+}+\eta^{A}+\eta^{E}+\eta^{D} \qquad ...(3)$$

where η^{+} is the positive increase in viscosity caused by long range electrostatic interactions; η^{E} is the positive increase due to the shape and size of an ion, η^{A} is the increase due to the alignment or the orientation of polar molecules by the ionic field, and η^{D} is the decrease in viscosity arising due to the distortion of the solvent structure by the ions.

Substituting Eq. (3) in (1) and eliminating the contribution due to the coulombic interaction from both, we get

$$\eta^{E}+\eta^{A}+\eta^{D} = \eta^{\circ}Bc$$

Therefore, *B* coefficient can be discussed in terms of these viscosity effects at a particular concentration and temperature.

The small lithium ion (Li^{+}) having high charge density strongly orient water molecules and its movement in the aqueous solution may be taken as the movement of a kinetic entity having a primary sheath of firmly attached water molecules. Also, water molecules beyond this inner layer are oriented to some extent and thus providing a positive value to η^{A}. The viscosity decrease due to distortion of solvent structure, i.e. η^{D}, is small for such ions. Therefore, for the sum $\eta^{E}+\eta^{A}>\eta^{D}$, *B* will be positive and fairly large.

The increase in *B*-coefficient with the increase in the concentration of DMF in solvent mixtures (Table 1) may be attributed to the larger size of the solvent molecules and also to the strong association

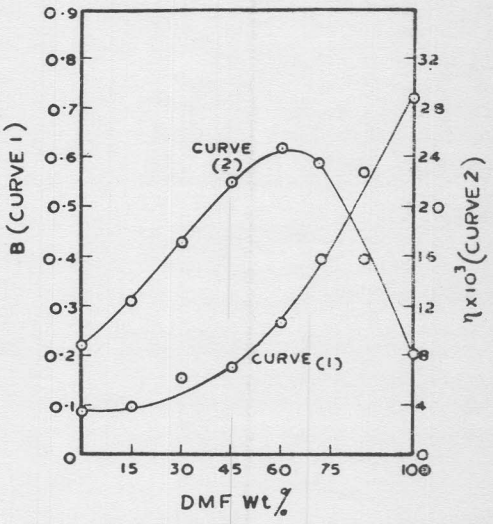

Fig. 1 — Viscosity data of DMF-water mixtures at 25°C (curve 2) and the plot of coefficient *B* of LiBr against the composition of the solvent (curve 1)

between water and DMF through multiple hydrogen bonding[12] and for solvated ions it would lead to larger value of η^E and η^A. Consequently B coefficient becomes larger and larger with the increase of DMF in the solvent mixture. This argument holds good for the ions of the intermediate size, like Na^+ for which $\eta^E+\eta^A \approx \eta^D$.

On the other hand, ions with greater crystal radii and small surface charge densities, like K^+, would have a weak orienting effect in the first layer. Therefore, η^E and η^A will be small. Also, there exists a considerable amount of distortion in the vicinity of such ions due to competition between the ionic field and bulk structure and consequently η^D will be large. Thus, $\eta^E+\eta^A<\eta^D$ and B will be negative for KBr in aqueous solution.

The results in Table 1 show that for potassium bromide B-coefficient in water-DMF mixtures first diminishes with increasing percentage of DMF and then begins to increase. Addition of small amounts of dimethylformamide enhances the solvent structure resulting in an increase in η^D due to the competition between the forces from the solvent structure in the bulk and the ionic field. Therefore, $\eta^E+\eta^A \ll \eta^D$ and B coefficient becomes more negative. With further addition of DMF, ions start orienting the solvent molecules and $\eta^E+\eta^A$ will begin to increase. The coefficient B will be zero when $\eta^E+\eta^A=\eta^D$ and will be positive when $\eta^E+\eta^A>\eta^D$.

From Table 1 it can also be seen that at any particular composition of the solvent the coefficient-B for LiBr>NaBr>KBr and this is in harmony with our discussion given above. Lithium ion having small size and higher charge density than the remaining two will be most structure forming in the series, hence its B value is greater.

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